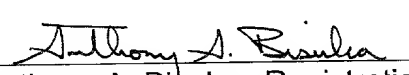


FORM PTO1390 OFFICE (REV 10-92)		U. S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK		ATTORNEY'S DOCKET NO 1999DE304	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)					
INTERNATIONAL APPLICATION NO. PCT/EP00/00834		INTERNATIONAL FILING DATE 02/02/2000 (02 February 2000)		PRIORITY DATE CLAIMED 24/02/1999 (24 February 1999)	
TITLE OF INVENTION For: Method for Producing (1,1':4,1'')-Terphenyl Compounds					
APPLICANT(S) FOR DO/EO/US Stefan SCHERER, et al.					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items under 35 U.S.C. 371: 1. <input checked="" type="checkbox"/> This express request to immediately begin national examination procedures (35 U.S.C. 371(f)). 2. <input checked="" type="checkbox"/> The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees as follows:					
CLAIMS	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
	TOTAL CLAIMS	11 - 20 =	20	X \$18.00	
	INDEPENDENT CLAIMS	2 - 3 =	0	X \$78.00	
	MULTIPLE DEPENDENT CLAIMS (if applicable)			+ 260.00	
	BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(4): <input checked="" type="checkbox"/> For filing with EPO or JP search report (37 CFR 1.492(a)(5))			\$ 860.00	860.00
	<input type="checkbox"/> International Preliminary Examination fee paid to USPTO (37 CFR 1.482)			670.00	
	<input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))			760.00	
	<input type="checkbox"/> Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO			970.00	
	<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Articles 33(2)-33(4)			96.00	
	Surcharge of \$130.00 for furnishing the National fee or oath or declaration later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 CFR 1.492(e)).				
	TOTAL OF ABOVE CALCULATIONS				= \$860.00
	SUBTOTAL				+ \$860.00
	TOTAL NATIONAL FEE				\$860.00
	Fee for recording the enclosed assignment (37 CFR 1.21(h)).				+ 40.00
	TOTAL FEES ENCLOSED				\$900.00
a. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>03-2060</u> in the amount of \$ <u>900.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.					
b. <input checked="" type="checkbox"/> The Commissioner is authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>03-2060</u> . A duplicate copy of this sheet is enclosed.					

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3.	X	A copy of the International Application as filed (35 USC 371(c)(2))	
		a.	is transmitted herewith.
		b.	is not required, as the application was filed in the US Receiving Office (RO/US).
		c.	X has been transmitted by the International Bureau.
4.	X	A translation of the Published International Application into English (35 USC 371(c)(2)).	
5.		Amendments to the claims of the International Application under PCT Article 19 (35 USC 371(c)(3)).	
		a.	are transmitted herewith (required only if not transmitted the International Bureau)
		b.	Have been transmitted by the International Bureau.
6.		A translation of the amendments to the claims under PCT Article 19 (35 USC 371(c)(3)).	
7.	X	An oath or declaration of the inventor (35 USC 371(c)(4)).	
8.	X	A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 USC 371(c)(5)).	
Other document(s) or information included:			
9.		An information Disclosure Statement under 37 CFR 1.97 and 1.98.	
10.	X	An assignment document for recording.	
10.1	X	Preliminary Amendment.	
10.2	X	A copy of the International Search Report.	
10.3	X	A copy of the International Preliminary Examination Report.	
10.4		Notification of the Recording of a Change	
11.		The above checked items are being transmitted after publication and the Article 20 communication but before twenty (20) months from the priority date	
12.		At the time of transmittal, the time limit for amending claims under Article 19:	
		a.	<input checked="" type="checkbox"/> has expired and no amendments were made.
		b.	<input type="checkbox"/> has not yet expired.
13.		Certain requirements under 35 USC 371 were previously submitted by the applicant on _____, namely:	
<div style="text-align: right;"> Date: <u>August 24, 2001</u></div> <div>Anthony A. Bisulca, Registration No. 40,913 (CUSTOMER NUMBER 25,255) Clariant Corporation 4331 Chesapeake Drive Charlotte, North Carolina 28216 Telephone: 704/395-6701 Facsimile: 704/395-6727</div>			

Docket No. 1999DE304

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re new U.S. patent application of :Attn: Box PATENT APPLICATION
Stefan SCHERER, et al. :
Serial No. To Be Assigned :
Filed: August 24, 2001 :
For: Method for Producing (1,1':4,1'')-Terphenyl Compounds

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, DC 20231

Dear Sir:

Preliminary to the examination of the above-identified application, please
amend the application as follows:

IN THE SPECIFICATION:

Page 1, before line 1, insert "METHOD FOR PRODUCING
(1,1':4,11'')-TERPHENYL COMPOUNDS".

Page 1, line 5, insert: --BACKGROUND OF THE INVENTION--.

Page 3, line 10, insert: --SUMMARY OF THE INVENTION--.

Page 12, line 12, insert --EXAMPLES--.

Page 20, line 1, insert: --CLAIMS--.

Page 20, line 1, insert: --ABSTRACT OF THE DISCLOSURE--.

IN THE CLAIMS:

Please amend the following claim:

Claim 3, line 1, delete "or 2".

Claim 4, line 1, delete "one or more of claims 1 to 3," and substitute therefore
--claim 1,--.

Claim 5, line 1, delete "one or more of claims 1 to 4," and substitute therefore
--claim 1,--.

Claim 6, line 1, delete "one or more of claims 1 to 5," and substitute therefore --claim 1,--.

Claim 7, line 1, delete "one or more of claims 1 to 5," and substitute therefore --claim 1,--.

Claim 8, line 1, delete "one or more of claims 1 to 7," and substitute therefore --claim 1,--.

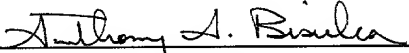
Claim 9, line 1, delete "one or more of claims 1 to 7," and substitute therefore --claim 1,--.

Claim 10, line 1, delete "one or more of claims 1 to 9," and substitute therefore --claim 1,--.

REMARKS

Entry of the above amendment is respectfully requested.

Respectfully submitted,



Anthony A. Bisulca
Registration No. 40,913

(CUSTOMER NUMBER 25,255)

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Facsimile: 704/395-6727

August 24, 2001

WO 00/50375

Description

Method for producing [1,1':4',1'']-terphenyl compounds

- 5 The present invention relates to a method for producing [1,1':4',1'']-terphenyl compounds substituted in the 4'' position.

4''-Alkoxyterphenyl-4-carboxylic acids whose alkoxy group contains an alkyl radical of medium chain length are used in conjunction with the
10 echinocandin B macrocycle as building blocks for producing active ingredients with antibiotic, in particular antifungal, properties.

These active ingredients display a novel principle of action and are therefore of particular interest (WO 94/25050 and EP 0 561 639).

15 The 4''-substituted p-terphenyl to be emphasized from the group thereof is 4''-n-pentoxy-[1,1':4',1'']-terphenyl-4-carboxylic acid, which leads, after coupling with the echinocandin B macrocycle, to a product with excellent properties.

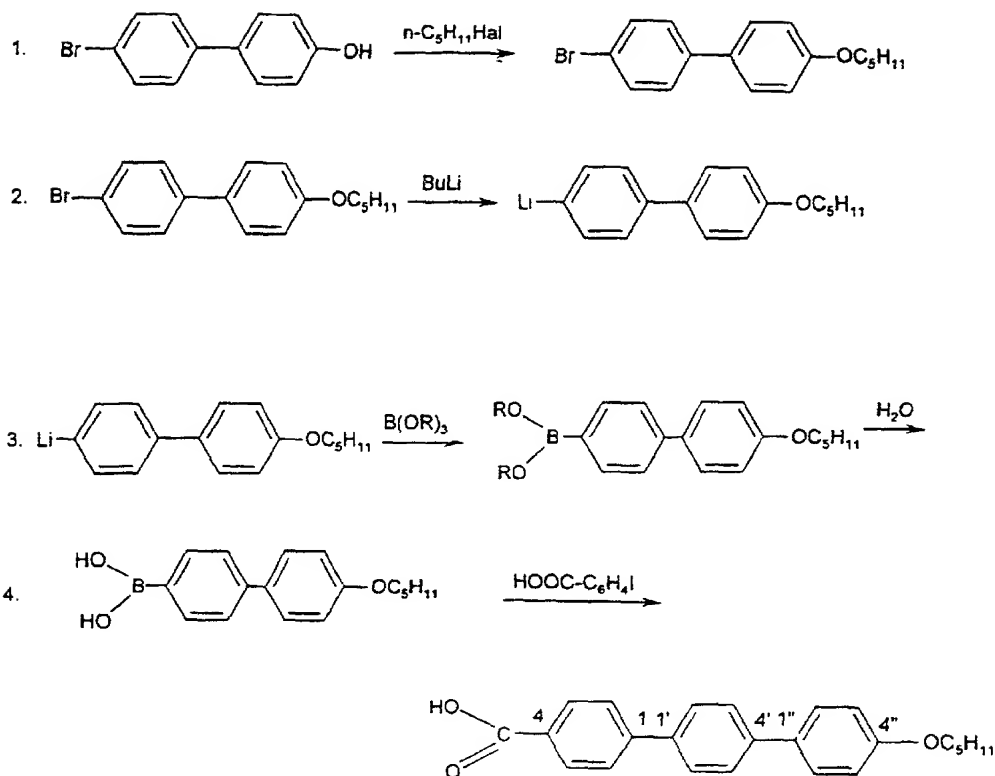
20 WO 94/25050 describes a multistage method for producing 4''-n-pentoxy-[1,1':4',1'']-terphenyl-4-carboxylic acid (cf. pages 28 and 29 part A, part B and part C).

25 In a first step, 4'-bromo-4-hydroxybiphenyl is reacted with an n-pentyl halide to give the corresponding 4'-bromo-4-n-pentoxybiphenyl. The 4'-bromo-4-n-pentoxybiphenyl is reacted in a second step with n-butyllithium at -78°C to form, by transmetallation, 4'-lithium-4-n-pentoxybiphenyl which, in another step likewise at -78°C, is reacted with
30 triisopropyl borate. Hydrolysis and work-up result in 4'-n-pentoxybiphenyl-4-boronic acid which is reacted in further steps with 4-iodobenzoic acid in a standard Suzuki coupling. The 4''-n-pentoxy[1,1':4',1'']-terphenyl-4-carboxylic acid is obtained as crude product which is purified by chromatography on silica gel.

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The mode of synthesis is depicted diagrammatically in simplified form below

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WO 94/25050 states yields only for the stages (part A and part B) up to formation of 4-(4-n-pentyloxyphenyl)phenylboronic acid. There is no statement of yield in part C, which relates to the production of 4''-n-pentyloxy-[1,1':4',1'']-terphenyl-4-carboxylic acid.

EP 0 561 639 discloses the production of methyl 4''-n-pentyloxy-[1,1':4',1'']-terphenyl-4 carboxylate using the aforementioned reaction steps 2, 3 and 4, employing methyl 4-iodobenzoate in place of 4-iodobenzoic acid in step 4. The yield of 4'-n-pentyloxybiphenyl-4-boronic acid is 44% and in the reaction thereof with methyl 4-iodobenzoate is 64% (cf. statements on page 26, table 15 and 16, in each case second line across), which means that the overall yield is only 28.2% based on 4'-bromo-4-n-pentyloxybiphenyl.

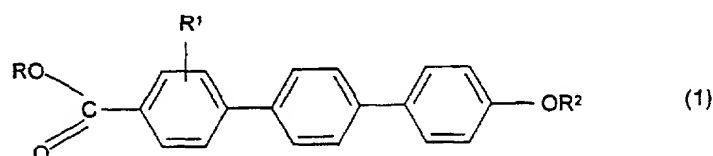
15

The method described above has several disadvantages. On the one hand, it is necessary to start from a very pure 4'-bromo-4-hydroxybiphenyl, which ought to contain the minimum amount of Br positional isomers in order to comply with the required isomer quality in the final product. On the other hand, the transmetalation in step 2 is rather complicated because it must be carried out at very low temperatures. If this reaction is not maintained in

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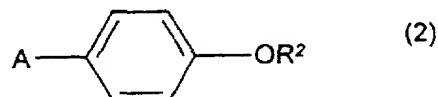
- a particular temperature range and/or if the reaction times are too long, the corresponding 4,4'''-di-n-pentoxy-[1,1':4',1'':4'',1''']-quaterphenyl is produced as a result of dimerization. This compound can, however, be removed from the desired final product only in a very complicated way. The reaction in step 3 is also carried out at very low temperature. A further disadvantage is that 4''-pentoxy-[1,1':4',1'']-terphenyl-4-carboxylic acid is evidently obtained as very impure crude product which must be purified by chromatography on silica gel.
- 10 In view of this, the object is to provide a method which avoids the disadvantages described above and can be carried out with acceptable effort.

- This object is achieved by a method for producing [1,1':4',1'']-terphenyl compounds with the formula

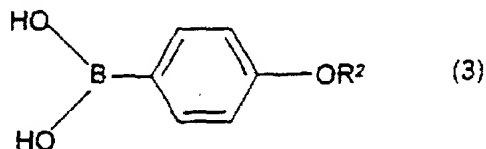


- in which R is hydrogen or a straight-chain or branched C₁-C₄-alkyl radical, in particular hydrogen, a C₁-C₂-alkyl radical or C(CH₃)₃, R¹ is hydrogen, a straight-chain or branched C₁-C₄-alkyl radical or a straight-chain or branched C₁-C₄-alkoxy radical, in particular hydrogen, a C₁-C₂-alkyl radical or C₁-C₂-alkoxy radical, preferably hydrogen, and R² is hydrogen, a straight-chain C₁-C₁₂-alkyl radical, an unsubstituted phenyl radical, a phenyl radical which is substituted by one or two C₁-C₄-alkyl groups or C₁-C₄-alkoxy groups, or a radical -(CH₂)_xOR³ in which x is an integer from 1 to 4 and R³ is a straight-chain or branched C₁-C₄-alkyl radical, in particular a straight-chain C₁-C₈-alkyl radical, an unsubstituted phenyl radical or a radical -(CH₂)_xOR³, in which x is an integer from 1 to 4 and R³ is a straight-chain or branched C₁-C₄-alkyl radical, preferably a straight-chain C₁-C₆-alkyl radical or a radical -(CH₂)_xOR³ in which x is an integer from 1 to 2 and R³ is a straight-chain or branched C₁-C₄-alkyl radical.

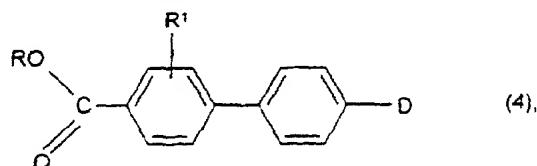
It comprises reacting a metal aryl of the formula



in which A is a monovalent metal or MeX, where Me is a divalent metal and X is Cl, Br or I, and R^2 is A or a trisubstituted silyl radical, or has the meaning indicated in formula (1), excepting hydrogen, with a boric ester at -80 to 40°C in the presence of an inert solvent, converting the reaction product by hydrolysis into a boronic acid of the formula

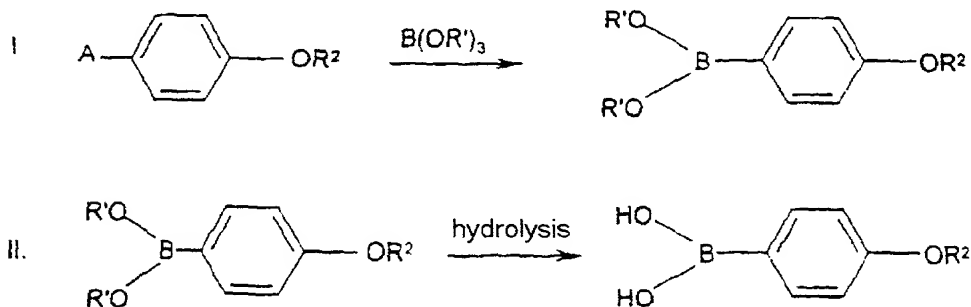


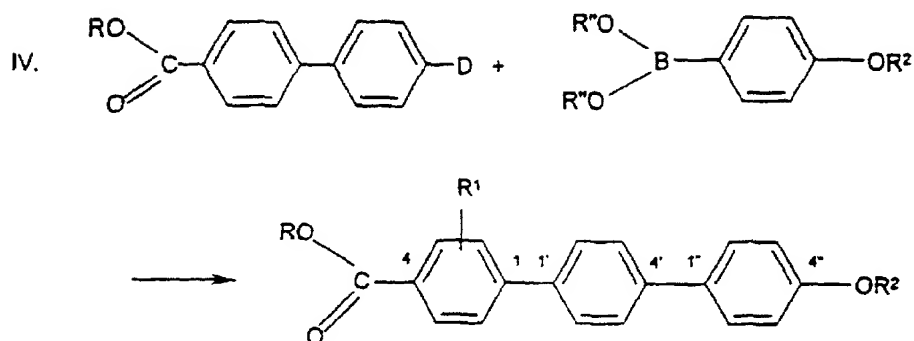
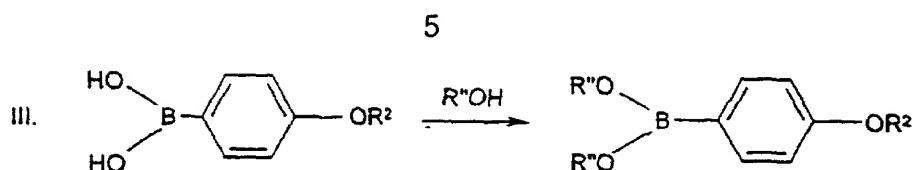
reacting the boronic acid, a boronic anhydride obtainable from boronic acid by elimination of water, or a mixture of boronic acid and boronic anhydride, with an alcohol, and reacting the boronic ester formed thereby with a biphenyl compound of the formula



in which R and R^1 have the meaning indicated in formula (1), and D is Cl, Br, I, $\text{O}_3\text{S}-\text{C}_n\text{F}_{2n+1}$, where n is an integer from 1 to 4, or N_2^+Y^- where Y^- is ClO_4^- , BF_4^- or HSO_4^- , at 40 to 180°C in the presence of a catalyst and of a polar solvent.

The method of the invention is depicted diagrammatically below in simplified form





The metal aryl of the formula (2) can be prepared by reacting a benzene derivative appropriately halogenated in the p position for example with Mg or an Li alkyl. There is no formation of a quaterphenyl compound which can be separated from the desired final product only with difficulty. The reaction of the metal aryl with boric ester does not in any case require the low temperatures indicated in WO 94/25050. Grignard compounds allow a reaction at distinctly higher temperatures than indicated in WO 94/25050.

A metal aryl of the formula (2) in which A is Li, Na, K, MgX or ZnX, in particular Li, MgX or ZnX and X is Cl, Br or I, in particular Cl or Br, is normally employed.

The method is particularly simple when a metal aryl of the formula (2) in which A is MgCl, MgBr or Mgl, in particular MgCl or MgBr, preferably MgCl, is employed.

As already mentioned above, a metal aryl of the formula (2) in which R^2 is A or a trisubstituted silyl radical, or has the meaning indicated in the compound of the formula (1), but in this case cannot be hydrogen, is employed.

If it is intended to produce a terphenyl compound of the formula (1) in which R^2 is hydrogen, it is possible to start from a metal aryl (2) in which R^2 is A

or the trisubstituted silyl radical, and to obtain the appropriate phenolic terphenyl compound by the subsequent work-up of the reaction product.

5 The trisubstituted silyl radical in the metal aryl is a radical $\text{SiR}^4\text{R}^5\text{R}^6$ in which the radicals R^4 , R^5 and R^6 are identical or different and are a phenyl radical or a $\text{C}_1\text{-C}_4$ -alkyl radical, in particular are the same and are a $\text{C}_1\text{-C}_4$ -alkyl radical. The silyl radical acts as protective group which can easily be eliminated after the reaction to form the appropriate phenolic group. A particularly suitable trisubstituted silyl radical is the $\text{Si}(\text{CH}_3)_3$ radical.

15 A boric ester $\text{B}(\text{OR}')_3$ in which R' is identical to or different from one another and is a straight-chain or branched $\text{C}_1\text{-C}_8$ -alkyl radical, a phenyl radical which is unsubstituted or substituted by one or two $\text{C}_1\text{-C}_4$ -alkyl groups or $\text{C}_1\text{-C}_4$ -alkoxy groups, in particular a straight-chain or a branched $\text{C}_1\text{-C}_4$ -alkyl radical, a phenyl radical which is unsubstituted or substituted by one or two $\text{C}_1\text{-C}_4$ -alkyl groups, preferably a straight-chain or branched $\text{C}_1\text{-C}_4$ -alkyl radical or an unsubstituted phenyl radical, particularly preferably a straight-chain or branched $\text{C}_1\text{-C}_4$ -alkyl radical, is employed.

20 Since the boric esters whose R' radicals are identical can be obtained particularly readily, the boric esters of the aforementioned type employed in a large number of cases will have identical R' radicals. Examples of such boric esters are trimethyl borate, triethyl borate, tri-*n*-propyl borate, 25 triisopropyl borate, tri-*n*-butyl borate and triisobutyl borate.

30 The reaction of the metal aryl with the boric ester is, as already mentioned at the outset, carried out at -80 to $+40^\circ\text{C}$, in particular -70 to 10°C , preferably -40 to 0°C . The inert solvent used is, for example, a dialkyl ether having 1 to 4 carbon atoms in each alkyl radical, a cycloaliphatic ether having 4 or 5 carbon atoms in the ring, for example tetrahydrofuran or 1,4-dioxane, a formaldehyde dialkyl acetal, a 1,2-dialkyl glycol ether having 1 to 4 carbon atoms in each alkyl radical, a mixture thereof or a mixture thereof with toluene, in particular a dialkyl ether having 1 to 4 carbon atoms 35 in each alkyl radical, tetrahydrofuran, a 1,2-dialkyl glycol ether having 1 to 4 carbon atoms in each alkyl radical, a mixture thereof or a mixture thereof with toluene, preferably tetrahydrofuran, dibutyl glycol ether, methyl tert-butyl ether, diethyl ether, diisopropyl ether, di-*n*-butyl ether, a mixture thereof or a mixture thereof with toluene.

The reaction of the boric ester with the metal aryl leads to a salt-like adduct (borate salt). After the reaction is complete, the reaction product which contains, where appropriate, the radical A or the trisubstituted silyl radical as radical R^2 , and any unreacted metal aryl which is still present, are decomposed by bringing the reaction mixture into contact with water or a water/ice mixture. The hydrolysis of the reaction product takes place very quickly, as does that of the metal aryl, because both the salt-like adduct and the metal aryl react very rapidly with water even at low temperatures. This leads to formation of the boronic acid (3), and salts derived from the reaction product and, where appropriate, from hydrolyzed metal aryl which is likewise still present are produced.

In order to dissolve salts, in particular basic salts, the resulting aqueous mixture is acidified, for example by adding a mineral acid, in particular hydrochloric acid or sulfuric acid. It is advisable to adjust a pH of from 0 to 4, in particular 0.5 to 3, preferably 1 to 2, to ensure complete dissolution of the salts.

A phase separation is then carried out, and the organic phase containing the inert solvent and the boronic acid is separated off. If required, the phase separation can be assisted by adding a suitable inert solvent, for example ether, methylene chloride, chloroform, toluene, chlorobenzene.

The organic phase which has been separated off is mixed with water in order to dissolve any salts still present, and the inert solvent and the solvent employed where appropriate to assist the phase separation are distilled off.

This results in the boronic acid as a solid. It is filtered off and dried. If the drying is carried out at temperatures ≥ 30 , in particular ≥ 50 , °C, the boronic acid starts to eliminate water to form the corresponding anhydride. Formation of the boronic anhydrides depends on the one hand on the temperature level, and on the other hand on the time during which the boronic acid is exposed to the temperature. High temperatures and long exposure times favor formation of boronic anhydrides.

If it is desired to obtain the boronic acid, it is advisable to carry out the drying at low temperatures and under vacuum.

It is also possible to hydrolyze the boronic anhydride for example with an aqueous alkali and to liberate the boronic acid by subsequent acidification of the aqueous solution containing salt of boronic acid.

5

In a large number of cases there is formation of a mixture of boronic acid and boronic anhydride. The boronic anhydride comprises cyclic anhydrides, in particular trimeric boronic anhydride. It is also possible in some circumstances for mixtures of anhydrides possibly to form. The boronic acid, the boronic anhydride and the mixture of boronic acid and boronic anhydride can be, if required, purified by recrystallization in a suitable solvent for example aliphatic, cycloaliphatic and/or aromatic hydrocarbons.

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In the following step, the boronic acid, the boronic anhydride or the mixture containing boronic acid and boronic anhydride is reacted with an alcohol. This esterification takes place by conventional methods. It is unnecessary to add a catalyst, for example an acid. It is possible that the boronic acid, the boronic anhydride or the mixture of boronic acid and boronic anhydride acts as catalyst. The esterification is normally allowed to proceed at 50 to 150°C, in particular 60 to 140°C.

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In order to favor the reaction, it is advisable to remove the water formed as a result of the esterification. This can take place, for example, by azeotropic distillation to remove water or by addition of dehydrating agents, for example orthoformic esters. Suitable entrainers for azeotropic removal of water are, for example, aliphatic or aromatic hydrocarbons, chlorinated aliphatic or aromatic hydrocarbons, ethers or ketones. Without making any claim to completeness, mention may be made of pentane, hexane, heptane, cyclopentane, cyclohexane, toluene, xylene, ethylbenzene, mesitylene, dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, chlorobenzene, dichlorobenzene, chlorotoluene or dichlorotoluene as entrainers.

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The alcohol employed is a C₁-C₈ alkyl alcohol, a C₂-C₆-alkane-1,2-diol, a C₃-C₆-alkane-1,3-diol, a C₄-C₆-alkane-1,4-diol or 1,2-dihydroxybenzene, in particular a C₁-C₈-alkyl alcohol, a C₂-C₆-alkane-1,2-diol or a C₃-C₆-alkane-1,3-diol, preferably a C₁-C₄-alkyl alcohol, a C₂-C₄-alkanediol or a C₃-C₅-alkane-1,3-diol.

Examples of alkyl alcohols are methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, n-pentanol, 2-methylpentanol, n-hexanol, 2-ethylhexanol, in particular methanol, ethanol, n-propanol, i-propanol, n-butanol and i-butanol.

5

Examples of suitable alkanediols are ethylene glycol, propane-1,3-diol and 2,2-dimethylpropane-1,3-diol (neopentyl glycol).

10

The reaction with the alcohol results in formation of the corresponding boronic ester, which is then reacted with the biphenyl compound of the formula (4) in the presence of a catalyst, of an acid-binding agent and of a polar solvent.

15

However, in place of the boronic ester, it is also possible to employ the boronic acid of the formula (3), the boronic anhydride obtainable from the boronic acid by elimination of water, or the mixture of boronic acid and boronic anhydride, in this reaction and thus dispense with the preparation of the boronic ester by reaction of the boronic acid, of the boronic anhydride or of the mixture of boronic acid and boronic anhydride with the

20

The reaction of the boronic ester or of the boronic acid, the boronic anhydride or the mixture of boronic acid and boronic anhydride takes place – as already mentioned – at 40 to 180°C, in particular 50 to 130°C, preferably 60 to 120°C. Acid-binding agents which can be used are amines, for example aliphatic amines, in particular trialkylamines, basic salts of organic and inorganic acids, in particular alkali metal salts and alkaline earth metal salts of organic and inorganic acids, for example Na acetate, K acetate, Na₃PO₄, K₃PO₄, NaHCO₃, KHCO₃, Na₂CO₃, K₂CO₃, MgCO₃, CaCO₃, or alkali metal oxides, alkali metal hydroxides, alkaline earth metal oxides, alkaline earth metal hydroxides, for example NaOH, KOH, Mg(OH)₂ or Ca(OH)₂.

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Very suitable acid-binding agents have proved to be alkali metal bicarbonates, alkali metal carbonates, alkaline earth metal bicarbonates and alkaline earth metal carbonates, in particular Na₂CO₃ and K₂CO₃, preferably Na₂CO₃. The biphenyl compound of the formula 4 which is particularly employed is that in which R is hydrogen or a straight-chain or

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branched C₁-C₄-alkyl radical, in particular hydrogen, a C₁-C₂-alkyl radical or C(CH₃)₃, preferably CH₃ or C(CH₃)₃, R¹ is hydrogen or a straight-chain or branched C₁-C₄-alkyl radical or C₁-C₄-alkoxy radical, in particular hydrogen, a C₁-C₂-alkyl radical or C₁-C₂-alkoxy radical, and D is Cl, Br, I or N₂⁺Y⁻, in particular Cl, Br or I, preferably Br or I.

It is possible to use as polar solvent a protic and aprotic dipolar solvent, in particular an alcohol, a sulfoxide, a sulfone, an amide and, where appropriate, water or a mixture thereof. Examples of alcohols are straight-chain or branched C₁-C₄-alkyl alcohols, ethylene glycol, polyethylene glycols of the formula HO-(CH₂-CH₂-O)_nH with n = 2 to 1 000 or mixtures of these alcohols with one another or with water, in particular ethylene glycol, mixtures of C₁-C₄-alkyl alcohols with ethylene glycol or with polyethylene glycols or with water, preferably mixtures of methanol and polyethylene glycols, methanol and ethylene glycol or butanol and water.

Examples of sulfoxides are dimethyl sulfoxide and diethyl sulfoxide.

Mention should be made of sulfolane, (thiolane dioxide) as representative from the sulfone series, and of dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide and N-methylpyrrolidone as representatives of the amide series.

In a number of cases it is also possible to employ mixtures of alcohols, sulfoxides, sulfolane and/or amides, which may also contain water where appropriate.

Suitable catalysts are palladium or a palladium or nickel compound. It is possible to employ Pd metal, Pd(0) complex compounds, Pd(II) complex compounds, Ni(0) complex compounds and Ni(II) complex compounds, in particular complex compounds which contain phosphines, preferably trisubstituted phosphines such as tri-n-butylphosphine, tri-tert-butylphosphine, triphenylphosphine (PPh₃).

Examples of Pd(0) complex compounds are Pd(PPh₃)₄, Pd(dba)₂.

Examples of Pd(II) complex compounds are PdCl₂(PPh₃)₂, PdBr₂(PPh₃)₂, PdCl₂(R"CN)₂PdBr₂(R"CN) with R" = phenyl, methyl, PdCl₂(dppf),

$\text{PdBr}_2(\text{dppf})$ with $\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene,
 $\text{PdCl}_2(\text{COD})$, $\text{PDBr}_2(\text{COD})$ with $\text{COD} = \text{cycloocta-1,5-diene}$.

- 5 Examples of $\text{Ni}(0)$ complex compounds are $\text{Ni}(\text{PPh}_3)_4$ and examples of
 $\text{Ni}(\text{II})$ complex compounds are $\text{NiCl}_2(\text{PPh}_3)_2$, $\text{NiBr}_2(\text{PPh}_3)_2$, NiCl_2dppf and
 NiBr_2dppf .

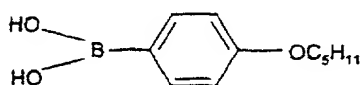
- 10 It is also possible to employ $\text{Pd}(\text{II})$ compounds or $\text{Ni}(\text{II})$ compounds, for
 example corresponding salts, together with the phosphines. In this case,
 the corresponding complex compounds are formed in situ.

Palladium compounds are particularly suitable, for example PdCl_2 ,
 $\text{Pd}(\text{acetate})_2$.

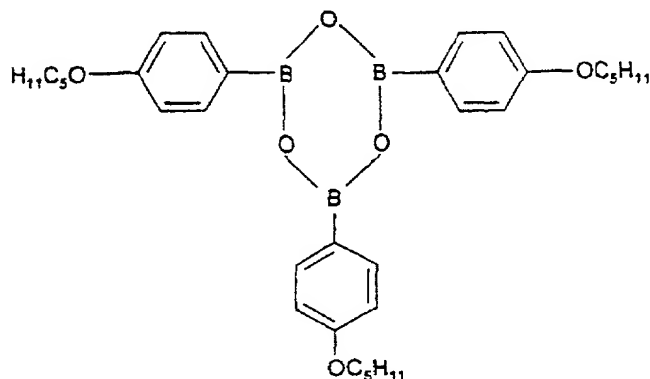
- 15 In the production of $[1,1':4',1'']$ -terphenyl-4-carboxylic acids ($\text{R} = \text{H}$ in
 formula (1)) it is advisable for the reaction product formed in the reaction of
 the biphenyl compound (4) to be treated with water and an acid, in
 particular a mineral acid, preferably HCl or H_2SO_4 , in order to bring about
 or complete hydrolysis of the salts which are formed. It has proved suitable
 20 in a number of cases to carry out the hydrolysis at elevated temperatures,
 for example at 30 to 100°C , in particular at 60 to 90°C .

The present invention also relates to the compounds
 4-n-pentoxyphenylboronic acid

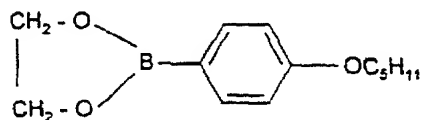
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trimeric 4-n-pentoxyphenylboronic anhydride

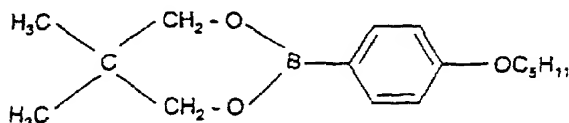


glycol ester of 4-n-pentoxyphenylboronic acid



and neopentyl glycol ester of 4-n-pentoxyphenylboronic acid

5



The following examples describe the invention in detail without restricting it.

Experimental part

10 Preparation of the starting material

Example A

Preparation of 4-n-pentoxyphenylmagnesium chloride (starting material).

- 15 134 g of a 30% strength solution of 4-pentoxyphenylmagnesium chloride in tetrahydrofuran are introduced together with 60.8 g of magnesium turnings into 178 g of tetrahydrofuran in a standard glass reaction vessel under an inert gas atmosphere and heated to boiling. One tenth of a solution of 497 g of 4-chlorophenyl pentyl ether in 450 g of tetrahydrofuran is added.
- 20 After the reaction starts, the remaining chloroaromatic compound is added dropwise over the course of 5 hours. After completion of the addition, heating under reflux is continued for 3 hours. After dilution with 675 g of tetrahydrofuran, excess magnesium is filtered off at room temperature under an inert gas atmosphere.
- 25 1930 g of a 30% strength solution of 4-pentoxyphenylmagnesium chloride in tetrahydrofuran are obtained.

Preparation of 4-n-pentoxyphenylboronic acid and 4-n-pentoxyphenylboronic anhydride

30

Example 1

Preparation of a mixture of 4-n-pentoxyphenylboronic acid and trimeric 4-n-pentoxyphenylboronic anhydride

390 g of tetrahydrofuran are introduced together with 437 g of trimethyl borate into a standard glass reaction vessel under an inert gas atmosphere and cooled to -20°C , and 3 000 g of 29% strength solution of 4-pentoxyphenylmagnesium chloride in tetrahydrofuran is added in such a way that the internal temperature does not exceed -15°C . After the addition is complete, the white suspension is cautiously added to a mixture of 1135 g of water and 1135 g of ice, and the resulting mixture is adjusted to pH 1-2 with 325 g of 60% strength sulfuric acid. After the magnesium salts have dissolved, the phases are separated, the upper product-containing organic phase (3200 g) is added to 3 l of water, and the tetrahydrofuran is substantially removed by distillation. This results in a white solid. The boronic acid is filtered off and dried at $50^{\circ}\text{C}/150$ mbar. This affords 540 g of 4-pentoxyphenylboronic acid as mixture with the trimeric anhydride, and the acid can be recrystallized from a hydrocarbon (hexane, cyclohexane) for further purification.

Example 2

Preparation of 4-n-pentoxyphenylboronic acid

The pure boronic acid is obtained from the originally obtained mixture of boronic acid with the trimeric anhydride by dissolving the mixture in excess sodium hydroxide at elevated temperature and, after cooling, precipitating the free boronic acid by adding 50% concentrated hydrochloric acid while cooling in ice.

Filtration and washing with water results in 4-n-pentoxyphenylboronic acid which is washed with water and has a melting point of $75-80^{\circ}\text{C}$ (pressed dry on a tile) and which forms the trimeric anhydride to a certain extent on drying (e.g. in a drying oven).

4-Pentoxyphenylboronic acid: IR spectrum

ν : 3334 (O-H), 2940, 1607, 1413, 1346, 1287, 1259, 1182, 1172, 1158, 1113, 1098, 1021, 997, 818 cm^{-1} .

Example 2a

Preparation of trimeric 4-n-pentoxyphenylboronic anhydride

The pure anhydride is obtained from the originally obtained mixture of boronic acid with the trimeric anhydride by either azeotropic dehydration of

the mixture in toluene and, after removal of the toluene, subsequent precipitation of the anhydride with cyclopentane, or drying the mixture in a drying oven in vacuo to constant weight at 50°C. The trimeric 4-n-pentoxyphenylboronic anhydride has a melting point of 102-103°C.

5

4-Pentoxyphenylboronic anhydride: IR spectrum

ν : 2932, 1604, 1414, 1381, 1368, 1356, 1346, 1305, 1292, 1270, 1247, 1173, 1021, 833 cm^{-1} .

10 Preparation of 4-n-pentoxyphenylboronic esters

Example 3

Preparation of glycol ester of 4-n-pentoxyphenylboronic acid

- 15 250 g of 4-n-pentoxyphenylboronic anhydride are dissolved together with 81 g of ethylene glycol by heating in 1 000 ml of toluene. The water produced in the esterification is removed azeotropically with a water trap. After the reaction is complete, firstly the toluene is distilled off and then the residue is fractionally distilled in vacuo. This affords 274 g of glycol ester of
- 20 4-n-pentoxyphenylboronic acid of boiling point 156°C/6 mbar, which solidifies after some hours (melting point 37-39°C).

Example 4

Preparation of neopentyl glycol ester of 4-n-pentoxyphenylboronic acid

25

- 505 g of 4-n-pentoxyphenylboronic anhydride are dissolved together with 274 g of 2,2-dimethylpropane-1,3-diol by heating in 2.5 l of toluene. The water produced in the esterification is removed azeotropically with a water trap. After the reaction is complete, the toluene is completely removed by
- 30 distillation in vacuo. 550 ml of cyclohexane are added to the residue, and the mixture is heated to boiling, filtered and cooled to room temperature. The precipitated 2,2-dimethylpropane-1,3-diol ester of 4-n-pentoxyphenylboronic acid is filtered off and dried at room temperature in vacuo. 595 g of 2,2-dimethylpropane-1,3-diol ester of 4-n-
- 35 pentoxyphenylboronic acid (neopentyl glycol ester of 4-n-pentoxyphenylboronic acid) are obtained with melting point 80-82°.

Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid from 4-n-pentoxyphenylboronic esters

Example 5

Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

- 5 162 g of 4'-iodobiphenyl-4-carboxylic acid are introduced together with
129 g of glycol ester of 4-n-pentoxyphenylboronic acid and 79.5 g of
sodium carbonate into 1.5 l of ethylene glycol and, while stirring vigorously,
350 mg of $\text{PdCl}_2(\text{PPh}_3)_2$ are added and the mixture is stirred at 80°C for
6 hours. The hot reaction mixture is cautiously poured into a mixture of
10 150 g of 37% strength sulfuric acid and 1 000 g of water, and the mixture is
heated at 90-100°C for 30 minutes. After filtration and washing with water,
the crude product is dried at 80°C/100 mbar and then recrystallized from
dimethylacetamide. This affords after drying 141 g (78%) of 4"-n-pentoxy-
[1,1':4',1"]-terphenyl-4-carboxylic acid with a purity of > 99%.

15

Example 6

Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

- 20 32.4 g of 4'-iodobiphenyl-4-carboxylic acid are introduced together with
25.8 g of glycol ester of 4-n-pentoxyphenylboronic acid and 15.9 g of
sodium carbonate into 300 ml of ethylene glycol and, while stirring
vigorously, 70 mg of $\text{PdCl}_2(\text{PPh}_3)_2$ are added, and the mixture is stirred at
120°C for 6 hours. The hot reaction mixture is cautiously poured into a
mixture of 30 g of 37% strength sulfuric acid and 200 g of water, and the
25 mixture is heated at 90-100°C for 30 minutes. After filtration and washing
with water, the crude product is dried at 80°C/100 mbar and then
recrystallized from dimethylacetamide. This affords after drying 25.2 g
(70%) of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid with a purity of
> 99%.

30

Example 7

Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

- 35 32.4 g of 4'-iodobiphenyl-4-carboxylic acid are introduced together with
25.8 g of glycol ester of 4-n-pentoxyphenylboronic acid and 15.9 g of
sodium carbonate into 300 ml of ethylene glycol and, while stirring
vigorously, 18 mg of PdCl_2 and 26.6 mg of PPh_3 are added, and the
mixture is stirred at 80°C for 6 hours. The hot reaction mixture is cautiously
poured into a mixture of 30 g of 37% strength sulfuric acid and 200 g of

water, and the mixture is heated at 90-100°C for 30 minutes. After filtration and washing with water, the crude product is dried at 80°C/100 mbar and then recrystallized from dimethylacetamide. This affords after drying 24.1 g (67%) of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid with a purity of

5 > 99%.

Example 8

Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

- 10 162 g of 4'-iodobiphenyl-4-carboxylic acid are introduced together with 129 g of glycol ester of 4-n-pentoxyphenylboronic acid and 79.5 g of sodium carbonate into 1.5 l of ethylene glycol and, while stirring vigorously, 17.5 ml of a Pd(dba)₂ solution are added and the mixture is stirred at 80°C for 6 hours. The hot reaction mixture is cautiously poured into a mixture of
- 15 150 g of 37% strength sulfuric acid and 1 000 g of water, and the mixture is heated at 90-100°C for 30 minutes. After filtration and washing with water, the crude product is dried at 80°C/100 mbar and then recrystallized from dimethylacetamide. This affords after drying 132 g (73%) of 4"-n-pentoxy-terphenyl-4-carboxylic acid with a purity of > 99%.

20

Preparation of the Pd(dba)₂ solution:

- Under an inert gas, 1.47 g of sodium tetrachloropalladate are suspended in 175 ml of ethylene glycol and heated to 60°C and, after addition of 3.65 g of dibenzylidene acetone (dba), stirred at 60°C for 15 minutes. This is
- 25 followed by addition of 7.5 g of sodium acetate and stirring at room temperature for a further 60 minutes, The dark-colored solution is employed as such.

Example 9

- 30 Preparation of 4"-n-pentoxy-[1,1':4',1"]- terphenyl-4-carboxylic acid

- 20.1 g of 4'-iodobiphenyl-4-carboxylic acid, 13.1 g of sodium carbonate and 21.4 g of glycol ester of 4-n-pentoxyphenylboronic acid are introduced into 260 g of dimethyl sulfoxide (DMSO) and, after addition of 160 mg of
- 35 PdCl₂(PPh₃)₂, heated at 100-110°C for 2 hours. The solid is filtered off at 40°C, washed with dimethyl sulfoxide and suspended in 100 ml of water. It is then heated to 80°C, and 47 g of 37% strength sulfuric acid are added dropwise over the course of 1 hour. The mixture is stirred at 80°C for a further 30 minutes, cooled at 40°C and filtered. Drying and crystallization

from dimethylacetamide results in 18 g (81%) of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid with a purity of > 99%.

Example 10

5 Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

32.4 g of 4'-iodobiphenyl-4-carboxylic acid are introduced together with 25.8 g of glycol ester of 4-n-pentoxyphenylboronic acid and 15.9 g of sodium carbonate into 300 ml of methanol/ethylene glycol 9:1 and, while stirring vigorously, 70 mg of $\text{PdCl}_2(\text{PPh}_3)_2$ are added, and the mixture is stirred under reflux for 6 hours. The hot reaction mixture is cautiously poured into a mixture of 30 g of 37% strength sulfuric acid and 200 g of water, and the mixture is heated at 90-100°C for 30 minutes. After filtration and washing with water, the crude product is dried at 80°C/100 mbar and then recrystallized from dimethylacetamide. This affords after drying 28.9 g (80%) of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid with a purity of > 99%.

Example 11

20 Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

162 g of 4'-iodobiphenyl-4-carboxylic acid are introduced together with 155 g of 2,2-dimethylpropane-1,3-diol ester of 4-pentoxyphenylboronic acid and 79.5 g of sodium carbonate into 1.5 l of ethylene glycol and, while stirring vigorously, 350 mg of $\text{PdCl}_2(\text{PPh}_3)_2$ are added and the mixture is stirred at 80°C for 6 hours. The hot reaction mixture is cautiously poured into a mixture of 150 g of 37% strength sulfuric acid and 1 000 g of water, and the mixture is heated at 90-100°C for 30 minutes. After filtration and washing with water, the crude product is dried at 80°C/100 mbar and then recrystallized from dimethylacetamide. This affords after drying 43.2 g (24%) of 4"-n-pentoxyterphenyl-4-carboxylic acid with a purity of > 99%.

Example 12

35 Preparation of 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid from 4-n-pentoxyphenylboronic acid

34.1 g (0.1 mol) of 95% pure 4'-iodobiphenyl-4-carboxylic acid are introduced together with 26 g (0.125 mol) of 4-n-pentoxyphenylboronic acid, 15.9 g (0.15 mol) of sodium carbonate and 70 mg of

bis(triphenylphosphine)palladium dichloride ($\text{PdCl}_2(\text{PPh}_3)_2$) into 300 ml of DMSO. The suspension is stirred at 80°C for 6 hours, the solid is filtered off, introduced into water, acidified with 37% strength sulfuric acid, heated at 95°C for 30 minutes and filtered again. Recrystallization from dimethylformamide (DMF) results in 22.1 g (61%) of 4"-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid.

Preparation of methyl 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylate from methyl 4'-iodobiphenyl-4-carboxylate

10

Example 13

Preparation of methyl 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylate

15 33.8g (0.1 mol) of methyl 4'-iodobiphenyl-4-carboxylate are introduced together with 29.3 g (0.125 mol) of glycol ester of 4-n-pentoxyphenylboronic acid, 70 mg of bis(triphenylphosphine)palladium dichloride and 15.9 g (0.15 mol) of sodium carbonate into 300 ml of DMF and stirred at 80°C for 12 hours. After filtration and washing with water, the
20 dried residue is recrystallized from DMF. This affords 20.5 g (45%) of methyl 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylate of melting point 248°C .

Comparative examples according to WO 94/25050 for preparing 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid

Comparative example 1

Preparation of 4'-n-pentoxybiphenyl-4-boronic acid from 4-bromo-4'-n-pentoxybiphenyl

30

31.9 g (0.1 mol) of 4-bromo-4'-n-pentoxybiphenyl are dissolved in 640 ml of tetrahydrofuran under a nitrogen atmosphere and cooled to -78°C , and 67 ml (0.11 mol) of 15% strength solution of n-butyllithium in hexane are added dropwise over the course of 2 hours. During this, the internal
35 temperature is kept in the range from -78°C to -65°C . After the addition is complete, the thick milky suspension stirred at -78°C for a further 15 minutes and then 25.5 ml (0.11 mol) of triisopropyl borate are added dropwise at -78°C over the course of 15 minutes. After the borate addition is complete, the resulting clear solution is stirred at -78°C for 15 minutes.

This is followed by a removal of the cooling bath and, after 40 minutes, the solution is adjusted to pH 2 with 100 ml of 2N hydrochloric acid. The phases are separated, the organic phase is washed with water and saturated brine and then the solvents are removed by distillation with addition of 200 ml of water. The precipitated solid is filtered off and dried. 25.8 g (91%) of 4'-n-pentoxybiphenyl-4-boronic acid of melting point 148-150°C are obtained.

Comparative example 2

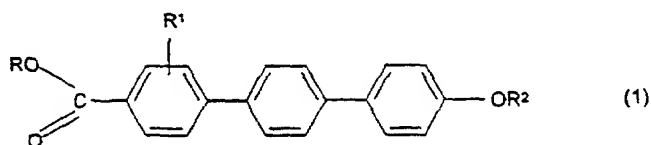
- 10 Preparation of 4"-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid from 4'-n-pentoxybiphenyl-4-boronic acid

25 g (0.088 mol) of 4'-n-pentoxybiphenyl-4-boronic acid and 21.8 g (0.088 mol) of 4-iodobenzoic acid are suspended under an inert gas atmosphere in a mixture of 270 ml of ethanol, 750 ml of toluene and 132 ml of a 2M sodium carbonate solution and, after addition of 5.08 g (4.4 mmol) of tetrakis(triphenylphosphine)palladium, heated under reflux for 18 hours. The gray-brown mixture is cooled, acidified and extracted with ethyl acetate. The organic phase is washed with water and saturated brine, dried (sodium sulfate) and filtered through Celite. Removal of the solvent results in 1.2 g of a solid which, however, according to HPLC analysis (comparison with reference substance) contains no 4"-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid at all.

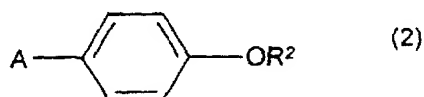
Evidently, no 4-n-pentoxy-[1,1':4',1"]-terphenyl-4-carboxylic acid has been formed by the synthetic route indicated in WO 94/25050.

Claims

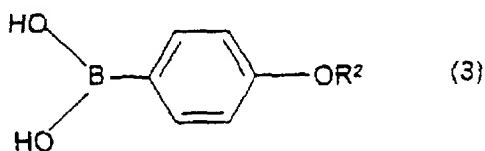
1. A method for producing [1,1':4,1'']-terphenyl compounds of the formula



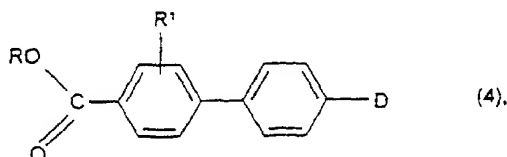
in which R is hydrogen or a straight-chain or branched C₁-C₄-alkyl radical, R¹ is hydrogen, a straight-chain or branched C₁-C₄-alkyl radical or a straight-chain or branched C₁-C₄-alkoxy radical and R² is hydrogen, a straight-chain C₁-C₁₂-alkyl radical, an unsubstituted phenyl radical, a phenyl radical which is substituted by one or two C₁-C₄-alkyl groups or C₁-C₄-alkoxy groups, or a radical -(CH₂)_xOR³ in which x is an integer from 1 to 4 and R³ is a straight-chain or branched C₁-C₄-alkyl radical, which comprises reacting a metal aryl of the formula



in which A is a monovalent metal or MeX, where Me is a divalent metal and X is Cl, Br or I, and R² is A or a trisubstituted silyl radical, or has the meaning indicated in formula (1), excepting hydrogen, with a boric ester at -80 to 40°C in the presence of an inert solvent, converting the reaction product by hydrolysis into a boronic acid of the formula



reacting the boronic acid, a boronic anhydride obtainable from boronic acid by elimination of water, or a mixture of boronic acid and boronic anhydride, with an alcohol, and reacting the boronic ester formed thereby with a biphenyl compound of the formula



in which R and R¹ have the meaning indicated in formula (1), and D is Cl, Br, I, O₃S-C_nF_{2n+1}, where n is an integer from 1 to 4, or N₂⁺Y⁻ where Y⁻ is

ClO_4^- , BF_4^- or HSO_4^- , at 40 to 180°C in the presence of a catalyst, of an acid-binding agent and of a polar solvent.

2. The method as claimed in claim 1, wherein a metal aryl of the formula (2) in which A is Li, Na, K, MgX or ZnX and X is Cl, Br or I is employed.

3. The method as claimed in claim 1 or 2, wherein a metal aryl of the formula (2) in which A is MgCl, MgBr or MgI is employed.

4. The method as claimed in one or more of claims 1 to 3, wherein a boric ester $\text{B}(\text{OR}')_3$ in which R' is identical to or different from one another and is a straight-chain or branched C_1 - C_8 -alkyl radical, or a phenyl radical which is unsubstituted or substituted by one or two C_1 - C_4 -alkyl groups or C_1 - C_4 -alkoxy groups is employed.

5. The method as claimed in one or more of claims 1 to 4, wherein a dialkyl ether having 1 to 4 carbon atoms in each alkyl radical, a cycloaliphatic ether having 4 or 5 carbon atoms in the ring, a formaldehyde dialkyl acetal, a 1,2-dialkyl glycol ether having 1 to 4 carbon atoms in each alkyl radical, a mixture thereof or a mixture thereof with toluene is employed as inert solvent.

6. The method as claimed in one or more of claims 1 to 5, wherein a C_1 - C_8 -alkyl alcohol, a C_2 - C_6 -alkane-1,2-diol, a C_3 - C_6 -alkane-1,3-diol, a C_4 - C_6 -alkane-1,4-diol or 1,2-dihydroxybenzene is employed as alcohol.

7. The method as claimed in one or more of claims 1 to 5, wherein the boronic acid, the boronic anhydride or the mixture of boronic acid and boronic anhydride is reacted in place of the boronic ester with the biphenyl compound of the formula (4).

8. The method as claimed in one or more of claims 1 to 7, wherein a biphenyl compound of the formula (4) in which D is Cl, Br, I or N_2^+Y^- is employed.

9. The method as claimed in one or more of claims 1 to 7, wherein palladium, a palladium compound or a nickel compound is employed as catalyst.

10. The method as claimed in one or more of claims 1 to 9, wherein an alcohol, a sulfoxide, a sulfone, an amide and, where appropriate, water or a mixture thereof is employed as polar solvent.

5

11. The compounds 4-n-pentoxyphenylboronic acid, trimeric 4-n-pentoxyphenylboronic anhydride, glycol ester of 4-n-pentoxyphenylboronic acid or neopentyl glycol ester of 4-n-pentoxyphenylboronic acid.

P. 04330 "2444662

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Method for producing (1,1':4,11'')-terphenyl compounds

the specification of which

☐ is attached hereto

☐ was filed on February 02, 2000 as International Patent Application PCT/EP00/00834

and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) for which Priority is Claimed:

Federal Republic of Germany, 19907904.8 of February 24, 1999

As a named inventor, I hereby appoint the following registered practitioner(s), respectively and individually, as my attorneys and/or agents, with full power of substitution and revocation, to prosecute this application, and transact all business in the U.S. Patent and Trademark Office:

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25255

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09914478-082401
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Date:

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